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This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

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Photolysis of Nitrogen Dioxide at 3660 and 4047 Å at 25°C*

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Nitrogen dioxide was irradiated at 3660 and 4047 Å at various pressures of NO_2, with and without CO_2, NO, and N_2 as added gases. The data indicate a primary dissociation at 3660 Å and shorter wavelengths corresponding to energies greater than the ON–O bond energy. At 4047 Å, the data are explained by an excited-molecule mechanism. Isotopic oxygen scrambling experiments at 4047 Å indicate the probability of reactions to produce oxygen atoms at that wavelength, but photolysis of NO_2 at trace concentrations and high inert-gas pressures indicates that these atoms are not derived from the unimolecular decomposition of the photoactivated molecule. The inhibition of the quantum yield by NO addition was pressure-dependent, lending further support to the premise that oxygen atoms are important in the mechanism at 4047 Å. It is postulated that the reaction $NO_2^*+NO_2 \rightarrow N_2O_3+O$ is the source of atomic oxygen.

INTRODUCTION

SEVERAL investigators have studied the photolysis of NO_2 under various conditions,[1–9] and a fairly consistent set of data has been evolved. Ford[8] has summarized most of the recent work, and has proposed mechanisms for the photolysis between 3100 and 3700 Å. The present study and that of Blacet, Hall, and Leighton[9] essentially substantiate Ford's mechanism in which NO_2 dissociates into NO and O in the primary process at wavelengths which correspond to the bond energy or greater. For the case where NO and O_2 are negligible, O atoms subsequently react with NO_2 which dissociates further via an activated NO_3 molecule as an intermediate. This mechanism is discussed in detail further on.

At wavelengths greater than about 3944 Å, which corresponds to 72.5 kcal/mole which is ΔE for the ON–O bond,[10,11] the data can be explained by an activated NO_2 molecule mechanism. Hall[4] reported that O^{18}–O^{18} was scrambled at 3100 Å to support the primary dissociation process at that wavelength; however, he did not observe scrambling at 4047 Å. Further work in this area was thought to be necessary in order to help clarify the mechanism at 4047 Å.

The present work was undertaken to obtain a systematic set of data at both 3660 and 4047 Å to help resolve the rather complex mechanisms that have been proposed. A further purpose of this study was to carry out experiments in the presence of nitrogen, since the results with this gas are directly related to the problems arising from nitrogen dioxide photochemistry in the atmosphere.

EXPERIMENTAL

The photolysis reactions were carried out in a quartz cell which was 10 cm long and 4 cm in diameter with a volume of 128 ml. The temperature of the system was controlled at 25±0.1°C by means of a thermostat from which water was circulated around the cell.

Quantities of NO_2, N_2, NO, and CO_2 were introduced into the cell by standard high-vacuum techniques. The vacuum system was free of mercury since diffusion-pump oil and Kel-F grease were used. The NO_2 pressure was measured by means of a silicone oil manometer (Dow Corning 704, $\rho=1.066$ g/cc) and also by its optical density at 4350 Å. The cell was designed to fit directly into a Cary Model 11 recording spectrophotometer. The extinction coefficient for NO_2 at 4350 Å was determined to be 1.73×10^5 ml mole^{-1} cm^{-1}, which is in agreement with the value reported by Hall.[4]

The cell was irradiated with light from a Bausch and Lomb monochromator (f/4.4, dispersion 16 Å/mm), with a General Electric BH6 mercury lamp as the light source. A slitwidth of 1.00 mm was used at both the entrance and exit slits. The total intensity of the beam emerging from the monochromator was measured with a calibrated Eppley line thermopile. The incident light was assumed to be proportional to the microvolt reading on a recording potentiometer. The absolute value of the light intensity was deter-

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[11] P. Brix and G. Herzberg, J. Chem. Phys. **31**, 1371 (1959).

TABLE I. Least-squares linear relationships in NO_2 photolysis.

Wavelength (Å)	Added gases	Equation of line (P in mm)	Average P_{NO_2} (mm)
3660	N_2	$1/\Phi_{NO_2}=0.499+1.81\times10^{-4}P_{N_2}$	5.84
3660	CO_2	$1/\Phi_{NO_2}=0.527+1.76\times10^{-4}P_{CO_2}$	6.12
3660	None	$1/\Phi_{NO_2}=0.52+0.233\ 1/P_{NO_2}$	
3660	N_2 (const. 1 atm)	$1/\Phi_{NO_2}=0.63+0.395\ 1/P_{NO_2}$	
3660	NO (N_2 const. 1 atm)	$1/\Phi_{NO_2}=0.61+0.326\ P_{NO}$	6.28
3660	NO (N_2 const. 0.1 atm)	$1/\Phi_{NO_2}=0.45+0.112\ P_{NO}$	6.01
4047	None	$1/\Phi_{NO_2}=1.28+0.260\ 1/P_{NO_2}$	
4047	N_2 (const. 1 atm)	$1/\Phi_{NO_2}=1.32+0.741\ 1/P_{NO_2}$	
4047	CO_2 (const. 1 atm)	$1/\Phi_{NO_2}=1.46+0.818\ 1/P_{NO_2}$	
4047	N_2	$1/\Phi_{NO_2}=1.35+3.60\times10^{-4}P_{N_2}$	5.69
4047	CO_2	$1/\Phi_{NO_2}=1.37+6.97\times10^{-4}P_{CO_2}$	8.81
4047	NO (N_2 const. 1 atm)	$1/\Phi_{NO_2}=1.22+1.97P_{NO}$	5.90
4047	NO (N_2 const. 0.1 atm)	$1/\Phi_{NO_2}=1.07+0.558P_{NO}$	6.24

mined by a standard uranyloxalate actinometric procedure.[12]

The NO_2 used in this work was Matheson Company research grade, and was purified by the method of Harris *et al.*[13] The purified NO_2 was stored as a white solid at -195°C and light was excluded from the storage bulb. Linde high-purity dry nitrogen was passed through ascarite and further dried by passage through $CaSO_4$ and $Mg(ClO_4)_2$. In the initial runs, the nitrogen was passed through electrolytic Cu at 800°C to remove possible O_2, and the resulting N_2 was distilled. Mass-spectrographic analysis showed that the latter purification steps were unnecessary, since impurities such as H_2O, O_2, and hydrocarbons were below the limit of detection by ordinary mass-spectrographic techniques (10–50 ppm). The CO_2 was obtained from the National Cylinder Gas Company and was approximately 99.5% pure. It was passed through $CaSO_4$, solidified, and pumped on. The middle portion of the sublimed sample was used in the experiments.

NO, obtained from Matheson, was purified by passing the gas through Ascarite, $CaSO_4$, $Mg(ClO_4)_2$, and a series of dry-ice–acetone traps. The remaining NO was distilled several times from liquid-nitrogen traps, each time retaining only the middle fractions. The resulting NO was stored as a gas. It was bluish white as a solid and blue as a liquid.

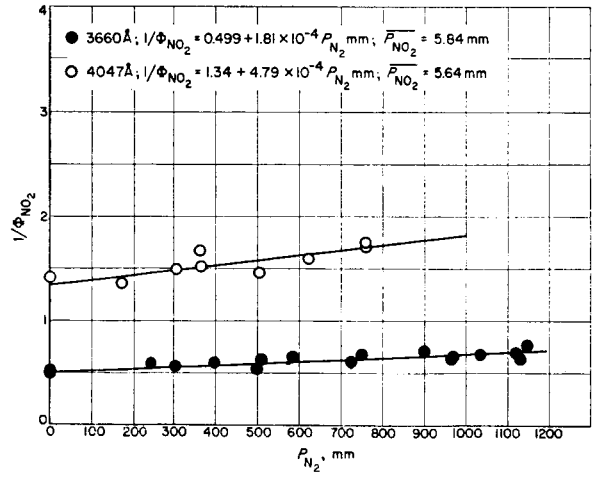


FIG. 1. Dependence of $1/\Phi_{NO_2}$ on the nitrogen pressure.

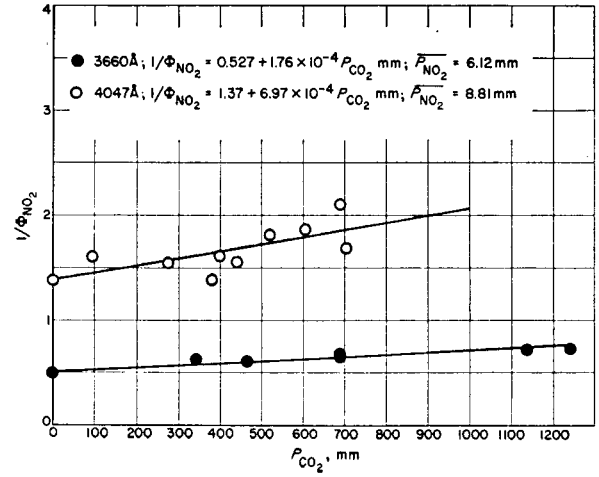


FIG. 2. Dependence of $1/\Phi_{NO_2}$ on the carbon dioxide pressure.

The isotopic oxygen used in the scrambling experiments was obtained from the Bio-Rad Laboratories (32nd and Griffin, Richmond, California). It contained 98.28% O^{18}, 0.47% O^{17}, and the balance O^{16}.

In a typical run, the desired gases were introduced into the sample cell while it was maintained at 25°C, and the concentration of the NO_2 was measured by means of the Cary spectrometer before and after the experiments. The incident-light intensity from the monochromator was measured by the thermopile output and recorded. The time of exposure was measured by means of a stopwatch which was calibrated in 0.1-sec increments. Quantum yields were calculated by the standard method, corrections for the dissociation of N_2O_4 and N_2O_3 being made where necessary. Correction was also made for the absorption of light

[12] W. A. Noyes, Jr. and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941), pp. 82–83.

[13] L. Harris, G. W. King, W. S. Benedict, and R. W. B. Pearse, J. Chem. Phys. 8, 765 (1940).

TABLE II. Results of oxygen scrambling experiments.

Wavelength Å	P_{NO_2} (mm)	P_{O_2} (mm)	P_{NO} (mm)	Before ratio 36/34	After ratio 36/34	Φ_{NO_2}	$\Phi_{O_2^{36}}$	Moles photo-produced O_2	Quanta absorbed/ min	Time in min
4047	8.47	0.71	...	25.0	23.56	0.70	0.062	1.74×10^{-6}	7.49×10^{16}	40
4047	9.05	0.55	...	25.0	9.77	0.65	0.021	6.27×10^{-6}	8.47×10^{16}	138
4047	8.41	0.71	...	25.0	8.24	0.73	0.037	6.16×10^{-6}	8.00×10^{16}	127
4047	8.50	0.67	...	20.8	15.18	0.78	0.035	3.07×10^{-6}	7.92×10^{16}	60
4358	8.88	0.39	...	20.6	20.8	0	0	0	0	60
4358	8.98	0.28	...	20.6	20.6	0	0	0	0	56
Dark	4.96	0.47	0.20	40.6	35.8	...	...	...	...	57
Dark	4.98	0.51	0.18	40.6	34.0	...	...	...	...	45

by N_2O_4 at 3660 Å using Hall's[4] extinction coefficients for NO_2 and N_2O_4.

The oxygen-scrambling experiments were carried out by introducing about 0.5 mm of the O_2^{36}-rich oxygen into the photolysis cell by means of a special vacuum-tight hypodermic syringe. The samples were irradiated as usual, and quantum yields were determined as described above. At the end of a run, O_2 was separated from the NO_2 and NO by freezing out the oxides in a liquid-nitrogen trap. The ratios of the O_2^{36} to O_2^{34} peaks were determined by ordinary mass-spectrographic analytical techniques. The values of the ratios after photolysis were compared with those before photolysis to estimate the extent of scrambling.

RESULTS

The quantum yield for NO_2 dissociation was measured at 3660 Å and at constant NO_2 pressure (~6 mm) as a function of CO_2 and N_2 pressure. The results are given in Table I and in Figs. 1 and 2. The data suggest linear relationships which are substantially in agreement with the pressure dependence reported by Blacet, Hall, and Leighton[9] for the effect of CO_2 at 3100 Å. In addition, the data indicate that the third-body efficiency of nitrogen is approximately the same as for CO_2 under these conditions.

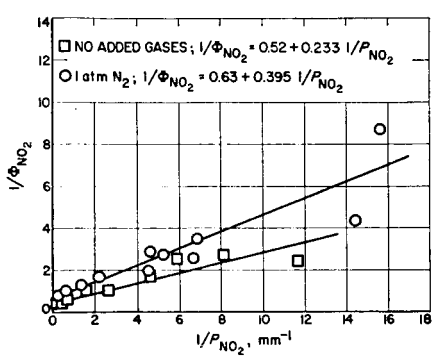


FIG. 3. Dependence of $1/\Phi_{NO_2}$ on $1/P_{NO_2}$ at 3660 Å.

Quantum yield measurements were also made with and without N_2, varying the NO_2 pressure. These results are shown in Table I and in Figs. 3 and 4. A plot of $1/\Phi_{NO_2}$ against $1/(NO_2)$ yields a straight line. However, the data at low pressures of NO_2 are subject to rather large errors because of the small concentration changes which are being measured. Therefore, Fig. 4 indicates a trend which must be verified by more precise measurements at pressures below about 0.1 mm of NO_2. The trend in the quantum yield toward zero as (NO_2) approaches zero is not anticipated by the present mechanism or by other experimental data.[6]

The mechanism of the photolytic dissociation of NO_2 at 4047 Å is not as clearly understood as that at 3660 Å and shorter wavelengths. Therefore, quantum yield measurements were made under a variety of conditions to help determine the mechanism at 4047 Å, and in particular, to attempt to distinguish between the postulated activated molecule[9] and the atomic-oxygen mechanism which obtains at shorter wavelengths.

Accordingly, a series of oxygen-scrambling experiments were performed using the change in the ratio of

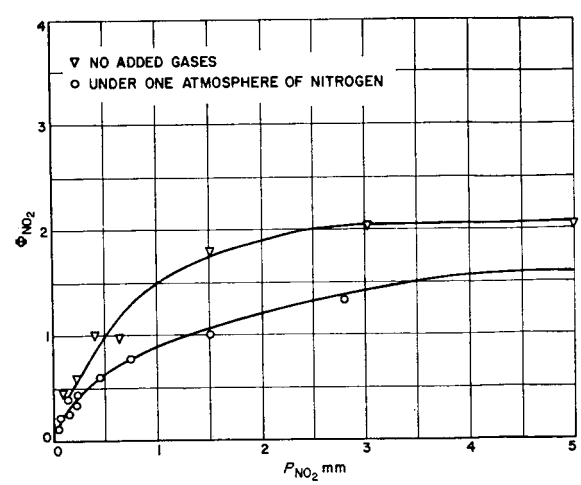


FIG. 4. Dependence of Φ_{NO_2} on the NO_2 pressure at 3660 Å.

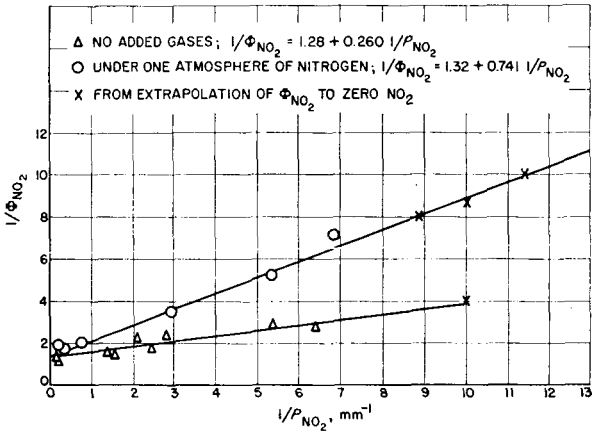


FIG. 5. Dependence of $1/\Phi_{NO_2}$ on $1/P_{NO_2}$ at 4047 Å.

O_2^{36} to O_2^{34}, as determined by mass spectrographic analysis, to follow the scrambling. The results of these experiments are summarized in Table II. The data show that scrambling is appreciable as long as there is a quantum yield for NO_2 dissociation. However, when the quantum yield approaches zero at 4358 Å, no measurable scrambling occurs. It is, therefore, evident that the scrambling phenomena are directly a result of the mechanism of photolysis.

The work of R. A. Ogg, Jr.,[14] suggests that scrambling can take place in the dark in mixtures of NO, NO_2, and O_2^{36}. The proposed mechanism for scrambling was

$$NO+O^{18}\text{–}O^{18}\rightleftarrows O^{18}\text{–}O^{18}NO^{16},$$

$$O^{18}\text{–}O^{18}NO+NO_2\rightarrow O^{18}NO^{16}+O^{18}O^{16}NO,$$

$$O^{18}O^{16}NO\rightarrow O^{18}\text{–}O^{16}+NO.$$

Therefore, two runs were made in the dark under

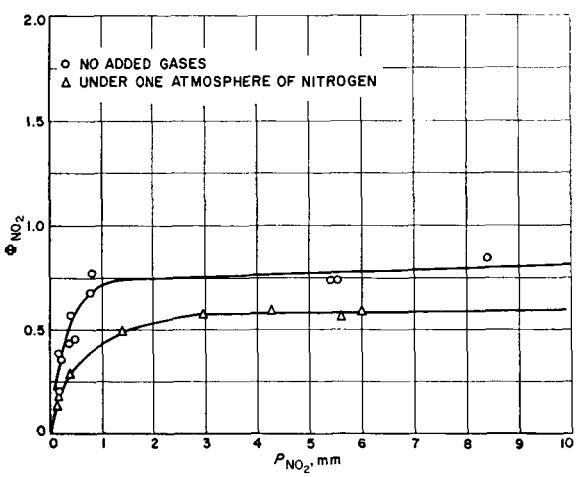


FIG. 6. Dependence of Φ_{NO_2} on the NO_2 pressure at 4047 Å.

[14] R. A. Ogg, Jr., J. Chem. Phys. **21**, 2079 (1953).

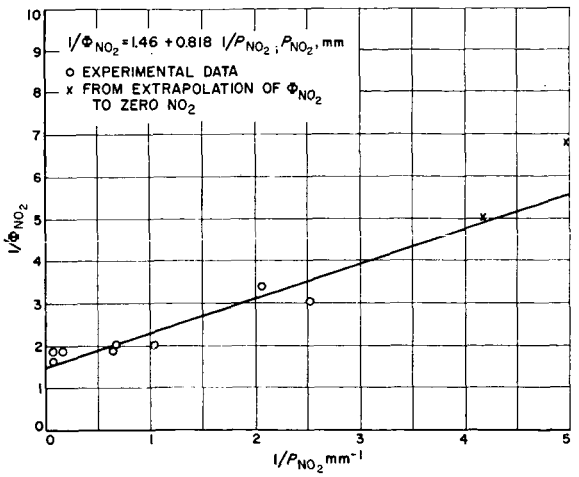


FIG. 7. Dependence of $1/\Phi_{NO_2}$ on $1/P_{NO_2}$ at 4047 Å and under 1 atm of carbon dioxide.

conditions simulating those in which photolysis took place. The NO concentration was approximately equal to the average which would be photoproduced during 1 h. Mass-spectrographic analysis showed that about 1×10^{-7} moles/liter of O_2^{36} were lost in each case during 1-h periods. However, in a comparable period, 3×10^{-6} moles/liter of O_2^{36} were lost during photolysis. This result indicates that oxygen atoms are probably responsible for most of the scrambling that was observed and that the dark reactions do not predominate.

Several series of experiments were carried out at 4047 Å to further determine the mechanism of photolysis. NO_2 was photolyzed at constant NO_2 pressure ($\sim$6 mm) while the N_2 and CO_2 pressures were varied from zero to about 1 atm. The data yield straight lines, the equations for which are given in Table I and shown in Figs. 1 and 2. In addition, experiments were performed with variable NO_2 pressure without any added gases and with N_2 and CO_2 each constant at one atmosphere pressure. Plots of $1/\Phi_{NO_2}$ as a function of $1/(NO_2)$ yielded straight lines. These data are shown in Table I and in Figs. 5 through 8.

A final series of experiments was carried out at 3660 and at 4047 Å with the addition of NO at partial

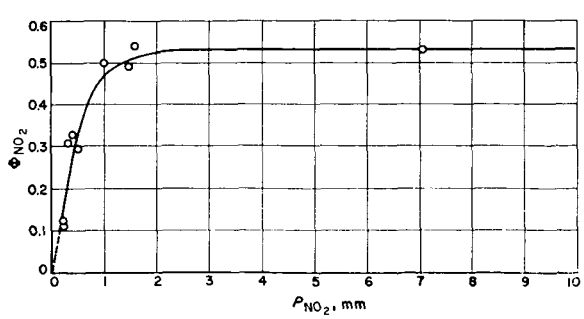


FIG. 8. Dependence of Φ_{NO_2} on the NO_2 pressure at 4047 Å and under 1 atm of carbon dioxide.

pressures low enough to avoid the back reaction:

$$2NO+O_2\rightarrow 2NO_2. \quad (1)$$

Photolysis with an atmosphere of nitrogen showed a greater inhibition of the quantum yield than that with 0.1 atm. In addition, the relative effects were the same at both wavelengths. This indicated that the influence of NO is pressure-dependent and could further support an oxygen atom mechanism at 4047 Å. The results of these experiments are also given in Table I and in Fig. 9.

DISCUSSION

A. Photolysis at 3660 Å

The mechanism of the photolytic dissociation of NO_2 at 3660 Å has been described by Ford[5–8] and reaffirmed by Blacet, Hall, and Leighton.[9] The mechanism may be written as follows:

$$NO_2+h\nu\rightarrow NO+O \qquad I_a, \quad (2)$$

$$O+NO_2\rightarrow NO+O_2 \qquad k_3, \quad (3)$$

$$O+NO_2\rightarrow NO_3^* \qquad k_4, \quad (4)$$

$$NO_3^*\rightarrow NO_2+O \qquad k_5, \quad (5)$$

$$NO_3^*+NO_2\rightarrow NO_2+O_2+NO \qquad k_6, \quad (6)$$

$$NO_3^*+M\rightarrow NO_3+M \qquad k_7, \quad (7)$$

$$NO+NO_3\rightarrow 2NO_2 \qquad k_8. \quad (8)$$

Assuming steady state for O and NO_3^*, the quantum-yield expression is:

$$\Phi_{NO_2}^{-1}=\tfrac{1}{2}+\frac{k_4k_7(M)}{2[k_3k_5+k_6(k_3+k_4)(NO_2)+k_3k_7(M)]}. \quad (9)$$

This mechanism indicates that photodissociation takes place at 3660 Å. Photodissociation would be expected since the Einstein unit at 3660 Å is 78.2 kcal

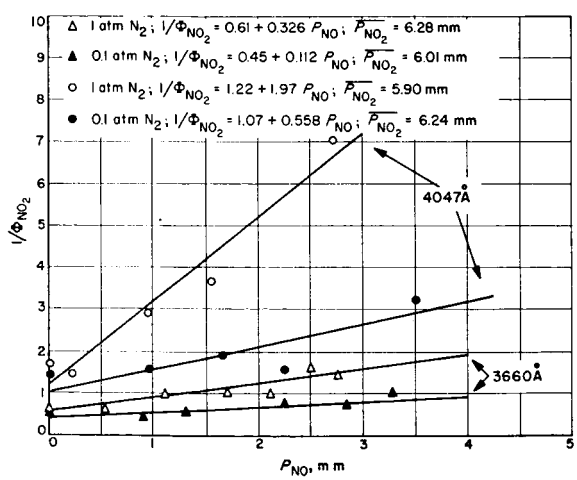


FIG. 9. Dependence of $1/\Phi_{NO_2}$ on the NO pressure.

TABLE III. Rate constants for the dissociation of NO_2 at 3660 Å.

Constant or ratio	Value	Remarks
k_3	2.1×10^9 liter mole^{-1} sec^{-1}	Reference 8
k_4	6×10^9 liter mole^{-1} sec^{-1}	Reference 8
k_5/k_6	0.002 mole liter^{-1}	This work
k_7/k_6	7.6×10^{-3}	From slope in Fig. 1 (M = N_2) and constants k_3, k_4, k_5/k_6 from this work and references 8 and 9.
k_6	5×10^8 liter mole^{-1} sec^{-1}	Reference 8
k_7	3.8×10^6 liter mole^{-1} sec^{-1}	From k_6, reference 8 and k_7/k_6 this work. (M = N_2)
k_8	3.4×10^9 liter mole^{-1} sec^{-1}	Reference 8

which is 5.7 kcal in excess of the ON–O bond energy. The problem would be settled uniquely if the fate of the O atoms were known. The assumptions that Reactions (3) and (4) take place seems reasonable and are not in conflict with the experimental evidence.

If the value of $k_7(M)$ is smaller than k_5, the term $k_3k_7(M)$ may be neglected and Eq. (9) yields a straight line when $1/\Phi_{NO_2}$ is plotted as a function of M. Lines of this form are shown in Figs. 1 and 2. The constants given in Table III are taken from earlier estimates and the slope of the 3660-Å line in Fig. 1. The constants derived from this work are in good agreement with those of earlier investigators.[8,9]

The mechanism proposed above fits the data fairly well for NO_2 pressures greater than about 2 mm. However, Eq. (9) requires that, as M approaches zero, $1/\Phi_{NO_2}$ approaches 0.5 and is not a function of the NO_2 pressure. Figures 3, 5, and 7 show that $1/\Phi_{NO_2}$ is a function of the NO_2 pressure below about 2 mm. This would require an extra term in Eq. (9) that is proportional to $1/(NO_2)$. Blacet, Hall, and Leighton[9] have proposed a wall deactivation to account for the phenomenon. However, since a similar effect is evident with and without added N_2 up to one atmosphere of N_2, wall reactions may not be the only explanation for the results.

If one adds the following steps to the mechanism,

$$NO_3^*+NO_2\rightarrow NO_3+NO_2, \quad (9a)$$

$$NO_3^*+\text{wall}\rightarrow NO_3+\text{wall}, \quad (9b)$$

the quantum yield expression becomes

$$\Phi_{NO_2}^{-1}=\tfrac{1}{2}+\frac{k_4k_{9a}(NO_2)+k_4k_7(M)+k_4k_{9b}}{2k_3[(k_6+k_{9a})(NO_2)+k_5+k_{9b}+k_7(M)]+2k_4k_6(NO_2)}. \quad (9c)$$

This relationship would account for the dependence

of the quantum yield on the NO_2 pressure when M is zero because of the term which includes the deactivation, (9b). When M is not zero, the term in $k_7(M)$ would be retained and the deactivation term in (9b) would go to zero. Therefore, the quantum yield would be a function of the NO_2 pressure under both conditions.

Using the constants in Table III and appropriate data from Table I, k_{9a} was calculated to be 5.4×10^7 liter mole^{-1} sec^{-1} and k_{9b} 1.6×10^5 sec^{-1} as calculated from Eq. (9c).

Quantum yield measurements are presently being made at NO_2 partial pressures well below 2 mm and the results will be reported in the near future.

B. Photolysis at 4047 Å

The photolysis of NO_2 at wavelengths greater than that corresponding to the energy of the ON–O bond (72.5 kcal/mole) has been a subject of great interest since predissociation cannot occur, and activated molecule mechanisms must be proposed. Blacet, Hall, and Leighton,[9] most recently, and Norrish,[3] earlier, have proposed such excited molecule mechanisms.

However, the work of Sato and Cvetanović[15] on the formation of organic oxides during the photolysis of NO_2 in the presence of olefins suggests that oxygen atoms are important in the reaction. The oxygen scrambling data shown in Table II give qualitative evidence that atoms are present during the photolytic process. The principal scrambling mechanism is probably:

$$O^{16}+O^{18}\text{–}O^{18}\rightarrow O^{16}\text{–}O^{18}+O^{18}, \qquad (10)$$

the O^{16} being derived from NO_2.

Molecular scrambling mechanisms, such as

$$O^{16}\text{–}O^{16}+O^{18}\text{–}O^{18}\rightarrow O^{16}\text{–}O^{18}+O^{16}\text{–}O^{18}, \qquad (10a)$$

$$O^{18}\text{–}O^{18}+O^{16}NO^{16}*\rightarrow O^{18}\text{–}O^{16}+O^{18}NO^{16}, \qquad (10b)$$

should not occur.

Further evidence for the presence of oxygen atoms is given in Fig. 9. The pressure dependence of the influence of NO on the inhibition of the quantum yield indicates that the following sequence of reactions may occur:

$$O+NO\rightarrow NO_2*, \qquad (11)$$

$$NO_2*+M\rightarrow NO_2+M, \qquad (12)$$

or

$$O+NO+M\rightarrow NO_2+M. \qquad (12a)$$

When Reaction (12a) is considered along with the mechanism given below, a rate constant, 12a, may be calculated from the data in Fig. 9. This calculation yields approximately 4×10^{11} liter^2 mole^{-2} sec^{-1}. This is an order of magnitude greater than the value 1.8×10^{10} liter^2 mole^{-2} sec^{-1} reported by Ford[8] and others. Since added NO has a greater effect than added N_2 when both are present, at least one other process is occurring and k_{12a} as calculated would be expected to be too high. However, the results support the premise that Reaction (12a) is one cause of the decrease in the quantum yield as a function of NO pressure.

Alternative reactions of NO with NO_2*,

$$NO+NO_2*\rightarrow NO+NO_2, \qquad (13)$$

are not a function of M, and may be assumed to be no more effective than the deactivation by N_2 or CO_2.

The data may be explained by the following mechanism:

$$NO_2+h\nu\rightarrow NO_2* \qquad I_a \qquad (14)$$

$$NO_2+NO_2*\rightarrow N_2O_3+O \qquad k_{15}, \qquad (15)$$

$$N_2O_3\rightarrow NO+NO_2 \qquad k_{16}, \qquad (16)$$

$$O+NO_2\rightarrow NO+O_2 \qquad k_{17}, \qquad (17)$$

$$NO_2*+M\rightarrow NO_2+M \qquad k_{18}, \qquad (18)$$

$$NO_2*+NO_2\rightarrow 2NO_2 \qquad k_{19}, \qquad (19)$$

$$NO_2*\rightarrow h\nu'+NO_2 \qquad k_{20}. \qquad (20)$$

Assuming steady state on O and NO_2*, the resulting quantum yield expression is

$$\Phi_{NO_2}{}^{-1}=\frac{1}{2}+\frac{k_{19}}{2k_{15}}+\frac{k_{18}(M)}{2k_{15}(NO_2)}+\frac{k_{20}}{2k_{15}(NO_2)}. \qquad (21)$$

Reaction (14) is probable since the ON–O bond energy is 72.5 kcal/mole and the energy equivalent to 4047 Å is only 70.7 kcal/mole. Therefore, dissociation would not be expected at this wavelength.

The manner in which dissociation follows the activation of the NO_2 molecule is, of course, the most impor-

TABLE IV. Rate-constant relationships for NO_2 photolysis at 4047 Å.

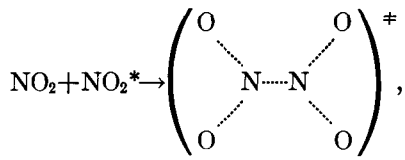
Constant or ratio	Value	Remarks
k_{17} (also k_3)	2.1×10^9 liter mole^{-1} sec^{-1}	Reference 6
k_{18}/k_{15}	4.1×10^{-3}	with M=N_2
k_{18}/k_{15}	1.23×10^{-3}	with M=CO_2
k_{19}/k_{15}	1.64	with M=N_2
k_{19}/k_{15}	1.92	with M=CO_2
k_{20}/k_{15}	2.8×10^{-5} moles liter^{-1}	with M=O
k_{19}/k_{18}	4.0×10^3	with M=N_2
k_{19}/k_{18}	1.56×10^3	with M=CO_2

[15] S. Sato and R. J. Cvetanović, Can. J. Chem. **36**, 279 (1958).

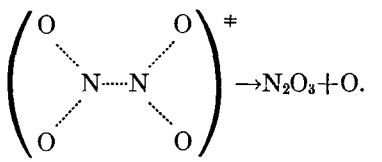
tant consideration in the mechanism. Blacet, Hall, and Leighton[9] proposed

$$NO_2+NO_2^*\rightarrow 2NO+O_2 \qquad (22)$$

to explain their data. However, this reaction does not explain the presence of oxygen atoms. Furthermore, since the quantum yield falls to zero at 4358 Å, a mechanism is required that is wavelength-dependent such that the energy necessary to break the bond is not available at 4358 Å and longer wavelengths. Reactions (15) and (16) satisfy the two requirements. If one assumes that the reaction proceeds by the formation of a transition complex such as the following:



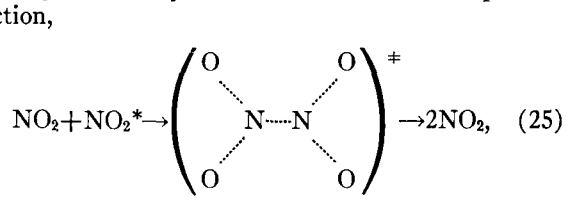
(23)



(24)

Approximately 13.3 kcal/mole are gained by the molecules in forming the N–N bond if the energetics of the $2NO_2 \rightleftarrows N_2O_4$ reaction may be taken as the model. The dissociation of N_2O_4 to form N_2O_3 and O requires about 76.7 kcal/mole. This energy may be obtained by adding the N–N bond energy to the energy supplied by the light. At 4047 Å, this gives about 84.0 kcal/mole, which is sufficient to permit reaction. At 4358 Å, the light supplied only 65.7 kcal/mole, yielding a total of 79.0 kcal/mole. If one makes the assumption that more than 2.3 kcal/mole and less than 7.3 kcal/mole in excess of the bond energy are needed for the dissociation, the proposed mechanism may be justified.

The question may be raised whether the competitive reaction,



(25)

would be so much faster than that indicated by Reaction (24), that it would predominate. The ratio of rate constants k_{19}/k_{15} should furnish a partial answer. This ratio is about 1.6 when M is N_2, indicating that dissociation may be appreciable relative to deactivation. It is realized that Reaction (25) is only one mode of deactivation which is implied by Reaction (19).

Since the data are not sufficiently sensitive to distinguish the effects of NO_3^*, and since the simplified mechanism does explain the data, references to the formation and subsequent reactions of NO_3^* have been omitted from the mechanism above. Inclusion of NO_3^* as a long-lived species leads to a complex quantum-yield expression which may or may not fit the data depending on the relative values of certain constants.

The fluorescence step [Reaction (20)] is proposed in accordance with the work of Baxter,[16] who determined the quenching of fluorescence at 4047 Å and at 4358 Å with and without H_2, N_2, CO_2, and O_2 as added gases. Quenching of fluorescence by NO_2 and by the added gases followed a Stern–Volmer relationship. Appreciable fluorescence was observed with up to 18.3 mm of NO_2. With added N_2, fluorescence was still observed up to 15.2 mm. These data indicate that fluorescence must be considered as a means of deactivating NO_2^* at all of the pressures of NO_2 used in this work. However, fluorescence may be unimportant at high inert-gas pressures.

Baxter assumed a mean lifetime of fluorescence of 10^{-7} sec. Although this leads to a very large collision diameter, 30×10^{-8} cm, it is not unusual for cases like this. A short lifetime would explain the lack of quenching up to appreciable pressures of NO_2.

Steps such as:

$$NO_2^*\rightarrow NO_2^{**}, \qquad (26)$$

$$NO_2^{**}\rightarrow h\nu''+NO_2, \qquad (27)$$

$$NO_2^{**}+M\rightarrow NO_2+M, \qquad (28)$$

$$NO_2^{**}+NO_2\rightarrow 2NO_2, \qquad (29)$$

were described by Blacet, Hall, and Leighton[9] and are certainly probable here. However, although they are implied, they are not capable of resolution by the present data.

The effect of fluorescence relative to photolysis may be demonstrated by the relative rate constants, k_{20}/k_{15}. Combination of the expressions $1/\Phi_{NO_2}$ vs $1/(NO_2)$ at M=O and at one atmosphere of nitrogen gives $k_{20}/k_{15}=0.52$ mm, which corresponds to 2.8×10^{-5} moles/liter. This is in good agreement with the value of 3×10^{-5} moles/liter given by Blacet, Hall, and Leighton.[9] A summary of rate-constant relationships is given in Table IV.

CONCLUSIONS

The results of this investigation indicate that the mechanism for the photolysis of NO_2 at 3660 Å explains the data for pressures of NO_2 above about 2 mm. Further experiments are necessary to determine the NO_2 pressure dependence of the quantum yield at pressures below 2 mm; investigating this region will probably show that the mechanism at 3660 Å is more complicated than previously reported.

[16] W. P. Baxter, J. Am. Chem. Soc. **52**, 3920 (1930).

The results at 4047 Å for the photolytic decomposition of NO_2 furnish strong evidence that oxygen atoms are important in the NO_2 dissociation and in the isotopic-oxygen scrambling.

This conclusion is based on the observations of Cvetanović[14] that oxygen atoms are available to form organic oxides when NO_2 is photolyzed in the presence of olefins, on the isotopic oxygen scrambling, on the pressure dependence of the inhibition of the quantum yield by NO, and by the wavelength dependence of the quantum yield.

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